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The reactivity of charged positive $Li_{1-n}[Ni_xMn_yCo_z]O_2$ electrodes with electrolyte at elevated temperatures using accelerating rate calorimetry

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HIGHLIGHTS

- Accelerating rate calorimetry is used to explore NMC/electrode reactivity.
- Single crystal NMC532 is less reactive than standard polycrystalline NMC532.
- Various coatings on NMC622 did little to limit reactivity.
- Reactivity increases strongly as the voltage increases.

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ABSTRACT

The reactivity between charged positive electrodes of (NMC) and traditional carbonate-based electrolyte (1.09 mol/kg $LiPF_6$ in ethylene carbonate (EC):ethyl methyl carbonate (EMC) (3:7 by weight)) with or without different electrolyte additives at elevated temperatures was methodically investigated using accelerating rate calorimetry (ARC). NMC samples studied included single crystal $Li_{1-n}[Ni_{0.5}Mn_{0.3}Co_{0.2}]O_2$ (SC-NMC532), Al_2O_3-coated $Li_{1-n}[Ni_{0.6}Mn_{0.2}Co_{0.2}]O_2$ (NMC622A) and $Li_{1-n}[Ni_{0.6}Mn_{0.2}Co_{0.2}]O_2$ coated with a proprietary high voltage coating material (NMC622B). The results from this work are compared to previous studies of other NMC materials made using the same methods to build a “library” of comparative results. The ARC results illustrate that the upper cut-off potential and sample morphology, influence the thermal stability of NMC materials, while additives and coatings have a smaller effect. Some outcomes of the work are that the single crystal morphology of NMC532 appears to lead to enhanced thermal stability compared to traditional NMC532 morphology and that NMC811 is significantly more reactive than all the other grades.

1. Introduction

$Li_{1-n}[Ni_xMn_yCo_z]O_2$ (NMC) positive electrode materials for lithium-ion batteries have high specific capacity, relatively low cost and can be used to make large format Li-ion cells with good safety characteristics [1]. Various NMC grades were compared by Kim et al. [2] in a wonderful review article where it was shown that specific capacity (to a fixed upper cutoff potential of 4.3 V increased with the Ni content while the thermal stability of the charged materials in electrolyte and the cycle life decreased with Ni content). Therefore, various tradeoffs must be made when selecting an appropriate positive electrode for a particular application.

Ma et al. [3] compared the reactivity of several kinds of NMC grades charged to different cut-off voltages with traditional carbonate-based electrolyte at elevated temperatures using accelerating rate calorimetry (ARC). According to that article, increasing Ni content and decreasing Mn and Co contents would generally decrease the thermal stability of charged NMC grades in electrolyte. The materials studied by Ma et al. [3] were “standard” NMC materials made from hydroxide precursors having traditional NMC morphology consisting of spherical secondary particles about 10 micrometers in diameter made up of secondary particles about 250 nm in diameter. The materials studied were not coated with thin layers of oxides or other materials to improve lifetime.

Since the time of the Ma et al. [3] work, single crystal NMC grades have become available [4] and it is very important to determine and verify if the single crystal morphology leads to thermal stability advantages over the traditional polycrystalline morphology [5]. Such experiments on single crystal NMC532 (called SC-NMC532 here) were

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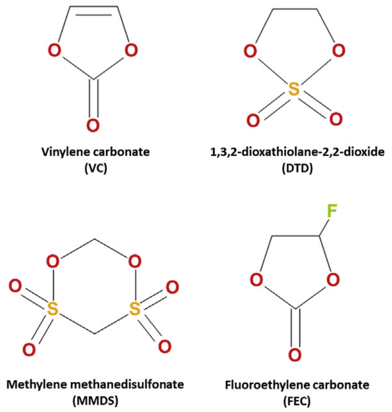

Fig. 1. Chemical structures of the electrolyte additives used in this work.

carried out here. In addition, coatings, like Al_2O_3 on NMC grades have also become more popular and it is important to determine how coatings impact thermal stability of charged electrode materials. Such experiments on Al_2O_3-coated NMC622 (called NMC622A here) and a proprietary coated NMC622 (called NMC622B here) are also carried out here.

In order to reduce the rates of parasitic reactions between charged electrodes and electrolyte, electrolyte additives are often utilized [6,7]. Vinylene carbonate (VC) is one of the most commonly used additives to optimize LIB performance [8,9]. Besides VC, ethylene sulfate (DTD) and methylene methanedisulfonate (MMDS) have also been studied for SC-NMC532 and NMC622 materials, respectively [10]. These electrolyte additives are able to extend lifetime and limit impedance increase for lithium ion batteries (LIBs) [8,11,12]. Electrolyte additives enhance cell performance by modifying the solid electrolyte interphase (SEI) at the graphite electrode or the passivation layer generated on the positive electrode [13–15]. Zuo et al. [16] found that the addition of MMDS to $LiCoO_2$/graphite cells modified the constituents of the passivation layer formed on the positive electrodes, which limited electrolyte oxidation. Sano et al. [17] demonstrated that there were compounds such as Li_2S and polymers like polyethylene oxide (PEO) in the SEI on the negative electrode in cells containing DTD. Electrolyte additives could therefore influence the reactivity of charged NMC materials with electrolyte at elevated temperature because they can modify the interphase between the charged electrodes and electrolytes [18]. The impact of electrolyte additives of reactivity is explored in this work.

Accelerating rate calorimetry (ARC) has been used to measure the reactivity between charged electrode materials and electrolyte at elevated temperatures, and it is able to distinguish the impact of various electrolyte additives as well [19]. In this paper, the reactivity of charged positive electrodes of SC-NMC532, NMC622A and NMC622B with electrolytes containing different electrolyte additives was methodically investigated and compared using ARC experiments. The additive systems probed were the binary electrolyte additive blends VC + DTD or VC + MMDS which have been shown to yield long lifetime cells based on SC-NMC532 and NMC622B, respectively [20]. Finally, the results from these new experiments are compared to the data collected by Ma et al. [3] on traditional NMC materials.

2. Materials and methods

2.1. Electrolyte selection

1.09 mol/kg lithium hexafluorophosphate ($LiPF_6$) (from BASF, purity 99.9%, water content 14 ppm) in ethylene carbonate (EC):ethyl methyl carbonate (EMC) (3:7 by weight, from BASF, purity 99.99%, water content < 20 ppm) was chosen to be the control electrolyte. For SC-NMC532 cells, the electrolyte being investigated contains 2% VC (from BASF, purity 99.97%) and 1% DTD (from Aldrich, purity 98%) (by weight). This electrolyte was selected based on the work of Li et al., who showed it to create SC-NMC532/graphite cells with excellent lifetime [20]. For NMC622A/graphite and NMC622B/graphite, the electrolyte being investigated contains 2% VC and 1% MMDS (from Guangzhou Tinci Co. Ltd, purity 98.70%) (by weight).

In experiments to measure the voltage to reach to the maximum capacity of three pouch cells, an electrolyte containing 2% fluoroethylene carbonate (FEC) (from BASF, purity 99.94%) by weight was used. Fig. 1 shows the molecular structures of the additives used in this study.

2.2. NMC pouch cell configuration

2.2.1. Characteristics of supplied dry cells

Dry (without electrolyte) SC-NMC532/graphite, NMC622A/graphite and NMC622B/graphite pouch cells balanced for 4.4 V operation were obtained from Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000). The SC-NMC532 used in these cells was described in the paper by Li et al. [4], while NMC622A and NMC622B were provided by Umicore (Chonan, Korea). NMC622A and NMC622B have an Al_2O_3 coating and a proprietary high voltage coating, respectively. The weight ratios of NMC to conductive carbon and polyvinylidene fluoride (PVDF) binder in the electrodes were 94:4:2, 96:2:2 and 96:2:2 for SC-NMC532, NMC622A and NMC622B, respectively. During the ARC testing at elevated temperatures, the reaction rate depends on the surface area of the interphase between the electrode materials and the electrolyte [21]. Table 1 presents the BET specific surface areas of all the samples. Fig. 2 shows the scanning electron microscope (SEM) images of the surfaces of the electrodes of the different positive electrode materials.

2.2.2. Electrode filling and formation of test cells

All of the pouch cells were vacuum sealed without electrolyte in China and then delivered to Canada. Before adding electrolyte, the cells were cut open in an argon-filled glove box and transferred to the antechamber for drying at 100 °C under vacuum for 14 h to remove residual water. All the sample cells were filled with 0.85 ml electrolyte. After filling, cells were vacuum-sealed using a compact vacuum sealer (MSK-115A, MTI Corp.). Cells were then charged to 1.5 V and held at the same voltage for 24 h, to allow for wetting. Then, all the cells for ARC test were placed in a temperature box at 40 ± 0.1 °C and charged at the current corresponding to C/20 to 3.5 V. Cells were then transferred into the glove box again, cut open to release the generated gas and then vacuum sealed. Then all the cells were charged at the current corresponding to C/20 to the corresponding upper cut-off voltage (4.1 V, 4.2 V, 4.3 V or 4.4 V) and held for 1 h, and then discharged to 3.8 V. If cells generated more than 0.1 ml of gas during the second step, they were degassed and sealed once more. The gas volume was measured using Archimedes principle with cells suspended from a balance while submerged in ultrapure water. The changes in the weight of the cell suspended in ultrapure water, before and after testing are directly related to the volume changes through the change in the buoyant force.

As Fig. 3 shows, cells used to measure the voltage to reach to the maximum capacity were placed in a temperature box at 40 ± 0.1 °C and charged at the current corresponding to C/20 to 4.8 V, and then discharged to 2.8 V. All the cells were then charged to 4.9 V then discharged to 4.4 V twice. After those two cycles, the cells were charged to

Table 1
Summary of the specific surface areas of the positive electrode materials in SC-NMC532/graphite, NMC622A/graphite and NMC622B/graphite pouch cells.

Material	SC-NMC532	NMC622A	NMC622B
Specific surface area (m^2/g)	0.28	0.24	0.24